

Device for treating a surface of a substrate, and a plasma source

The present invention relates to a device for treating a surface of a substrate, comprising a treatment chamber for receiving the substrate therein, at least one plasma source for generating a plasma, which plasma source is connected to the treatment chamber, and comprising inlet means for admitting at least one reactant into a flow path of the plasma, wherein the plasma source comprises at least one cathode and at least one anode between which a system of at least one cascade plate is received, which at least one cascade plate is provided with an opening for passage of the plasma. The invention 10 also relates to a plasma source.

A device of the type stated in the preamble is for instance known from European patent application EP 297.637 and is becoming increasingly popular for the purpose of surface modifications of substrates. Such a modification can consist of deposition of an 15 optionally crystalline layer, optionally masked etching of a top layer of the substrate, a surface activation or, conversely, a surface passivation and the like. Such preparations occur frequently as semiconductor technology steps in a process of manufacturing for instance integrated semiconductor circuits, solar cells and image reproduction systems. However, in order to manufacture larger products such as sunglasses and contact lenses, 20 there is also a need for a controllable process with which the substrate surface can be accurately modified. These include not only wafer-like substrates but also so-called reel-to-reel processes, wherein a substrate guided through the reaction chamber at a normally continuous speed is processed in fully continuous manner.

25 A processing device on the basis of a plasma provides the advantage that a wide variety of reactants can hereby be presented and a high rate of flow achieved in controlled manner. A drawback of the plasma reactors used nowadays is however the relatively limited cross-section of the plasma beam, which is particularly noticeable in the case of larger substrates. Since in many applications constant efforts are being made to scale up 30 the substrate size, such as the wafer diameter in semiconductor processes and the image diagonal in image display panels, this drawback will be increasingly perceived as

restricting. Attempts to enlarge the cross-section of the passage opening to allow passage of a wider plasma beam pass have thus far foundered because the system is thus found to become unstable or does not allow start-up at all. Furthermore, a larger plasma beam will still only have its intended effect locally and over a relatively limited part of 5 the substrate, while there is precisely a need for a plasma source with which the whole substrate, or at least a large part thereof, is covered.

Instead of scaling-up the plasma beam itself, resort has therefore been made to the application of a number of plasma sources per treatment chamber, so that it is possible 10 to process the substrate simultaneously with this same number of plasma beams. In practice such a system is only found to be stable if each plasma source is herein also provided with a separate, stabilized electric power supply and with a separate inlet for a reactant, which has the effect of greatly increasing cost price. In addition, due to the application of separate, independently controlled beams, the homogeneity of the 15 treatment over the full surface is difficult, if not impossible, to achieve in such a known device.

The present invention has for its object, among others, to provide such a device which obviates these and other drawbacks to at least a significant extent.

20 In order to achieve the intended object, a device of the type stated in the preamble has the feature according to the invention that the at least one cascade plate is provided with a number of passage openings, wherein corresponding openings of successive cascade plates are substantially mutually aligned, and that between the at least one cathode and 25 the system of cascade plates there is a plasma space present which is in open communication with the passage openings in the at least one cascade plate of the system. A plasma beam flows through each passage opening in the cascade plates during operation. A plurality of plasma beams is thus generated with a plasma source in order to simultaneously cover a correspondingly larger area on the substrate.

Surprisingly, it has been found that such an increase in the number of openings per cascade plate, otherwise than enlarging a single opening, has at least no noticeable adverse effect on the stability of the plasma. The plasma is thus moreover spread over a larger surface area, whereby a distributed plasma is as it were obtained which can

5 actually cover an entire surface of a substrate or at least a large part thereof. Since according to the invention use is made of a common plasma space preceding the system of cascade plates and the thereby achieved division into separate plasma beams, it is possible to suffice with a single, likewise common electric power supply and reactant inlet for the whole. An increase in cost price, as in a device with separate plasma

10 sources, can hereby be avoided to at least a significant extent. And, otherwise than in the use of separate plasma sources to generate the same number of plasma beams, application of the invention does not necessarily result in an essentially larger size thereof. On the contrary, the invention thus provides the option of realizing a plasma source for a distributed plasma while retaining compactness.

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In a preferred embodiment the device according to the invention is characterized in that the passage openings are ordered at least almost equidistantly from each other in the at least one cascade plate. A uniform distribution of the plasma beams over the surface of the cascade plates is thus obtained, with a view to the desired relative uniformity of the 20 beams. In practice use can be made for this purpose of for instance passage openings which lie with their centre on the corner points of an imaginary isosceles triangle, a square, a regular pentagon, hexagon and so on, wherein in the configurations which occur the space within such a mathematical figure also provides space for placing additional passage openings.

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Particularly good results have been achieved with a further particular embodiment of the device according to the invention, characterized in that the at least one cascade plate is provided with at least three passage openings. The openings in the plates can herein take a congruent form, but can also intentionally be of different shape or size.

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In a further preferred embodiment the device according to the invention has the feature that the inlet means are adapted to admit the reactant, on a side of the adjacent cascade plate remote from the plasma space, into flow paths of the plasma extending through the openings. The cathode(s) situated on the opposite side of the relevant cascade plate are thus shielded from the reactant by this same cascade plate. Particularly in the case of strongly reactive reactants, this enhances the integrity and lifespan of the cathode(s), whereby the device can remain operational for longer.

In a further particular embodiment the device according to the invention has the feature that at least one cathode is provided per passage opening in the adjacent cascade plate. By applying a number of openings in the cascade plates, for passage of the same number of plasma beams, the maximum plasma flow which can be drawn through the device will also increase. In order to enable the device to produce such an increase in plasma flow, particularly at the initial ignition of the device, at least one cathode is thus also arranged per added opening, so that the total plasma flow running through the device can be spread over sufficient cathodes.

Alternatively, a further particular embodiment of the device according to the invention is characterized in that less than one cathode is provided per passage opening in the adjacent cascade plate. At least some of the cathodes are thus shared between passage openings. Although the plasma flow is thus drawn from one common cathode through all the sharing passage openings, and this total flow is limited to the maximum supply capacity of this cathode, this has the advantage that the plasma space, which would otherwise be required for additional cathodes, can be omitted, thus resulting in a more compact construction, while the generated plasma can nevertheless be provided distributed over a considerable surface area. The plasma flows which can thus be achieved have been found in practice to be sufficient for many applications, while, surprisingly, a stable plasma is created in all of the passage openings sharing in this manner.

The invention also relates to a plasma source for generating a plasma, comprising at least one cathode and at least one anode, in addition to a system located therebetween of at least one cascade plate with a passage opening for a generated plasma, characterized in that the at least one cascade plate is provided with a number of passage openings, 5 each intended for throughfeed of a separate plasma flow, and that the openings are in open communication with a common plasma space which is received between the system and the at least one cathode.

The invention will be further elucidated hereinbelow on the basis of an embodiment 10 and an associated drawing. In the drawing:

- figure 1 shows a cross-section of an embodiment of a device according to the invention for treating a surface of a substrate;
- figure 2 shows a detail view of the part A of the plasma source of figure 1;
- figure 3A shows a front view of a cascade plate as applied in the plasma source of 15 the device of figure 1; and
- figure 3B shows a further embodiment of a cascade plate applicable in a device according to the invention.

The figures are purely schematic here and not drawn to scale. For the sake of clarity some dimensions in particular are (highly) exaggerated. Where useful, corresponding 20 parts are designated in the figures with the same reference numeral.

Figure 1 shows schematically the construction of a device for treating a surface of a substrate using or supported by a plasma according to an embodiment of the invention, a so-called plasma reactor. The plasma reactor comprises a housing 1 having on one 25 side a plasma source 13 and on the other a treatment chamber 3 for receiving therein a substrate 9 for treating. Plasma source 13 is connected to treatment chamber 3 via a plasma inlet. A plasma 8 generated by the plasma source can thus enter treatment chamber 3. Plasma 8 is herein directed at a main surface of the substrate 9 for treating, which is held in position by a substrate holder 10. Substrate holder 10 is held at a 30 temperature of between 70 and 1000 Kelvin by means of a cooling channel and/or built-in heating element (not shown). Holder 10 is electrically insulated relative to housing 1

so that holder 10 can be part of one or more extra discharges in the plasma treatment space 3. The plasma inlet preferably comprises a nozzle 5, an end of which debouches in plasma treatment space 3 and spreads the plasma a little over the substrate so as to thus cover a larger surface area.

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In the case a liquid or gaseous reactant is used, injection hereof takes place in plasma generator 13 via a gas inlet 11, see also figure 2. In addition, an inlet 12 is present for a suitable flushing gas which is injected in order to enable (semi-)continuous operation of the reactor. The flushing gas can consist of a random mixture of gases which, after 10 separation, do not produce fragments which could damage components of plasma generator 13, such as for instance inert gasses such as argon, helium, hydrogen and nitrogen. The ratio of the injected quantities of flushing gas and the reactant, expressed in m³/sec. at STP (Standard Temperature and Pressure) gas equivalent, i.e. 273 Kelvin and 1 Bar, lies typically between 1 and 1000 and usually between 8 and 400. The liquid 15 or gaseous reactant for instance contains a compound which can be separated and ionized, such as halogenated hydrocarbons.

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In order to carry out a controlled plasma treatment free of undesired by-products in plasma 8, a pressure above 0.1 Bar, preferably between 0.1 and 3.5 Bar, is maintained 20 in plasma generator 13 during operation, while treatment chamber 3 is preferably held at a pressure below 0.05 Bar (= 5 kPa) and in particular below 200 Pa, independently of the controllable pressure of the injected flushing gas and the reactant. For this purpose the device is provided with pump means with which the plasma treatment chamber 3 can be evacuated via a controllable valve 16 and two outlets 14,15. The pump applied 25 here comprises for instance a Roots-blower (not shown) in combination with an oil diffusion pump connected to outlet 15. Such a diffusion pump is also able to hold housing 1 constantly at a lower pressure of 3-10 Pa when the device is not in operation, in order to thus prevent fouling.

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In order to control and regulate the plasma 8 a preferably water-cooled skimmer can be part of plasma treatment space 3. The diameter of plasma 8 can be influenced, if

desired, using such a skimmer. For a further fine-tuning and confinement of the plasma, magnet coils 7 are moreover arranged in this embodiment with which a magnetic field can be created around plasma 8 as desired.

5 Plasma 8 is generated with a plasma source 13 in which a system of cascade plates 80 is applied between one or more cathodes 20 and one or more anodes 5. The system here comprises nine such successive cascade plates 80, made of copper, with a total length of about 40-80 millimetres. In this embodiment supersonic nozzle-shaped anodes are applied with which deposition of material at undesired locations in the treatment space

10 3 can be avoided. Such an anode 5 is formed by a releasable insert provided with a fitting pressure ring 51 with which it is pressed into cooling plate 30. The insert has a conical cavity open on either side, a diameter of which increases gradually in a direction toward the substrate. The cavity has an inlet opening with a diameter which is a little larger than the diameter of the plasma channel 95 connecting thereto, and then tapers

15 into an outlet opening so that the channel widens by an angle of for instance over 10 degrees relative to a central axis of channel 95. An inner wall of the insert must be given an extremely smooth finish to a surface roughness of less than about 0.1μ (micron).

20 According to the invention each cascade plate 80 herein comprises more than one passage opening 85, see also figure 3A, wherein corresponding passage openings 85 are substantially aligned in successive cascade plates so as to thus form a corresponding number of plasma channels 95. Plasma channels 95 provide separate flow paths for the generated plasma from the nozzle-like anode 5 to cathodes 20. A high-energy plasma

25 arc into which a reactant can be carried and ionized can thus be drawn between anodes 5 and cathodes 20.

In normal operation the potential over the arc preferably amounts to between 20 and 200 V, in particular between 50 and 150 V. The plasma 8 is started by reducing the pressure in the arc and applying an ignition voltage of about 1000 Volts until ignition takes place and a large current of for instance more than 10 A begins to flow. The

pressure is then increased rapidly, i.e. for instance within 5 seconds, until the desired value is reached and a stable arc is formed after passing through all intermediate discharge phases. Finally, the channels 95 together carry an electric direct current of 20 to 200 A from anodes 5 to cathodes 20. The plasma 8 in channels 95 can be observed 5 via a window 41 in a window cap 42 provided for this purpose. Window cap 42 also contains inlet 12 for possible supply of a flushing gas.

In this embodiment, see figure 3, cascade plates 80 each comprise three such passage 10 openings 85 with a substantially congruent circular cross-section with a diameter of 2-6 millimetres, in this embodiment about 5 millimetres. Situated preceding the first cascade plate 80 there is according to the invention a common plasma space 90 which is in open communication with the various passage openings 85 in plates 80. This gives the plasma the opportunity, after being ignited, to spread over the different channels so that three separate beams, and in the case of more openings an even greater number of 15 separate beams, are formed. Although in this embodiment the passage openings are arranged completely regularly and mutually equidistant on the corner points of an imaginary equilateral triangle, they can in principle be spread relatively at random over the surface of the plates, and can optionally be given a different design and/or differ from each other in order to thus form a plasma distributed over practically the whole 20 surface thereof. Figure 3B shows an example of such an alternative embodiment of a cascade plate 80, without this being in any way limitative. The separate plasma beams enter treatment chamber 3 parallel to each other so as to cover the surface of substrate 9 completely or at least for the greater part, as if they were the jets from a shower head.

25 Because the plates 80 are exposed during operation to high temperatures in the order of 10,000 Kelvin and high energy densities in the plasma, it is important to cool the plates with a suitable cooling agent. Provided for this purpose in the plates, in particular close to the passage openings, are channels 87 through which can be pumped a suitable cooling liquid, such as for instance water. This ensures an adequate heat discharge, and 30 thereby cooling of the cascade plates. Plates 80 are mutually separated and electrically insulated by means of a system of O-ring seals 82, spacer rings 81, for instance of PVC,

and central rings 83 of boron-nitride. Seals 82 ensure that a pressure between 0.05 and 5 Bar is possible in the plasma arc. Central rings 83 have a white colour, whereby they reflect the light emitted by the plasma and thus prevent the O-rings 82 from melting as a result of the absorption of plasma light. The packet of cascade plates 80 is held firmly 5 together using a number of bolts 35 which are placed through bores 84 provided for this purpose in the cascade plates and which protrude through a cooling plate 30 in which the anodes 5 are held. Using bolts 36 the packet is thus connected firmly to cooling plate 30. Bolts 35 are provided with insulating sleeves and rings (not shown) in order to avoid electrical contact with plates 80,30.

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Plasma source 13 comprises in this embodiment two identical cathode tips 20 made from an alloy of 2% thorium in tungsten. Cathode tips 20 are mounted in hollow holders 21, through which cooling water is supplied and discharged via conduit 22. Holders 21 are at least partially encased in a sleeve 23 made of for instance quartz, and 15 are held in place by a screw connection 24 which provides space for a rubber seal (not shown) and fixedly clamps the holder 21 in sleeve 23 in vacuum-tight state. The placing and the number of cathode tips 20 in plasma space 90 can be chosen comparatively freely and requires no adjustment, or hardly any, to the number and the position of channels 95. The chosen number is here therefore lower than the number of openings 20 85 so as to save the costs and space of cathode tips, so that a more compact and cheaper construction is possible, although if desired an equal or a greater number can also be chosen compared to the number of plasma channels 95 in order to enable durable production of more electric current. The device can thus be adapted to a specific application.

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At the end of each channel 95 is situated an anode 5 in the form of a relatively easily removable conical insert which can be pressed by means of a pressure ring 51 into a complementary opening formed for this purpose in a water-cooled plate 30. Cooling plate 30 is for instance manufactured from copper and is provided internally with a meandering or spiralling liquid channel between an inlet 31 and an outlet 32. Cooling 30 water is carried to the cooling plate via inlet 31 and to outlet 32 via the cooling channel.

Said inserts are for instance made from low-oxygen copper. Cooling plate 30 is electrically insulated from housing 1 by an insulating sleeve 33.

At the position of the first two cascade plates 80 of the system is situated the inlet 11 for a gaseous reactant. This inlet 11 debouches on a side of the first cascade plate 80 remote from cathode 20 between the two mutually facing surfaces of this pair of cascade plates, see figure 2. One of the two plates 80 is provided for this purpose with a channel 86 through which the gaseous reactant can be injected into plasma channels 85,95. For this purpose a recess with a thickness of about 0.1 mm is arranged in the central boron-nitride ring 83. Cathode 20 is thus shielded by the first cascade plate 80 from the sometimes strongly reactive gaseous reactant, in order to thus protect cathode 20 from corrosion and premature wear. Channel 86 is arranged such that it nowhere makes contact with cooling channel 87 in the same cascade plate 80.

For the injection of liquid reactants into plasma channels 95 a comparable passage can be provided, wherein injection channel 86 then comprises at least one capillary vessel. Such a capillary vessel is also arranged such that nowhere is contact made with the cooling channel 87 in the same plate. The diameter of the capillary vessel is preferably chosen such that supplied liquid, which is supplied at a higher pressure than the pressure prevailing in plasma channels 95, only evaporates at the end of the capillary vessel where it debouches in the central area between the plates 80 where openings 85 and the plasma channels running therethrough are situated.

In addition to gaseous and liquid reactants, the device also provides the option of applying reactants from a solid phase. For this purpose the device comprises in or close to a flow path of plasma 8 a cathode 61 which is flanked on either side by an anode 60. In this embodiment both are disposed at a certain distance of for instance roughly 10 centimetres from a central axis of the formed plasma beams 8. Both the cathode 61 and the anode 60 are electrically insulated from housing 1. Under the influence of the electrical field which is created between the main anode 5 and cathode 20, an auxiliary discharge will be induced between auxiliary anode 60 and auxiliary cathode 61. When

this discharge is energized at a voltage typically between 200 and 1000 Volts, and with a current density of typically 50 to 1000 mA/cm², a sputtering discharge will take place between anode 60 and cathode 61, wherein solid particles are released from the cathode which will subsequently mix with plasma 8. By manufacturing cathode 61 from a solid reactant, the solid reactant material can thus be sputtered from the cathode and introduced into the plasma. In this embodiment the cathode 61 is manufactured from copper so as enable copper to be produced as solid reactant. Situated in cathode 61 is a cooling channel 62 which can be coupled to cooling means via conduits (not shown) in order to allow the temperature to be maintained, if necessary, at an acceptable level.

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The complete device is coupled to pump means during operation and continuously pumped out thereby via connections 14,15, wherein a pressure difference is preferably created between plasma source 13 and treatment chamber 3 such that the plasma can be as it were extracted through anode nozzle 5. The pump speed must herein be chosen such that the expansion in sub-atmospheric plasma treatment space 3 assumes a supersonic character. In that case the equilibrium of the plasma is 'frozen'. Three-particle and radiation-recombination processes are generally too slow to allow a substantial reduction in the number of reactive plasma particles to occur in the short time then remaining until the substrate for processing is reached. Since both the gas and the electron temperature in the plasma have a value of about 10,000 Kelvin, the sound speed is roughly 1750 m/s. This limits the mass flow, because the sound velocity is passed at a position with the smallest diameter, in most cases in nozzle 5 or the end of plasma channel 95. With the device according to the invention an exceptionally high flux of the reactant can thus be achieved, wherein the treatment is carried out simultaneously over the whole surface of the substrate, or at least a large part thereof, in particularly uniform and controlled manner.

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Although the invention has been further elucidated above in detail with reference to only a single embodiment, it will be apparent that the invention is in no way limited thereto. On the contrary, many other variations and embodiments are possible for the

person with ordinary skill in the art without him being required to depart from the scope of the invention.